

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
19 April 2001 (19.04.2001)

PCT

(10) International Publication Number
WO 01/27046 A1

(51) International Patent Classification⁷: **C03C 3/062**,
3/068, 3/12, 4/00

IA 52403 (US). NORDINE, Paul, C.; 735 Carriage Way,
Deerfield, IL 60015 (US).

(21) International Application Number: PCT/US00/28567

(74) Agents: FASSNACHT, Harold, J. et al.; Bullwinkel Part-
ners, Ltd., 19 South LaSalle Street #1300, Chicago, IL
60603 (US).

(22) International Filing Date: 13 October 2000 (13.10.2000)

(25) Filing Language:

English

(81) Designated State (*national*): JP.

(26) Publication Language:

English

(84) Designated States (*regional*): European patent (AT, BE,
CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC,
NL, PT, SE).

(30) Priority Data:

60/159,380

14 October 1999 (14.10.1999)

US

Published:

— With international search report.

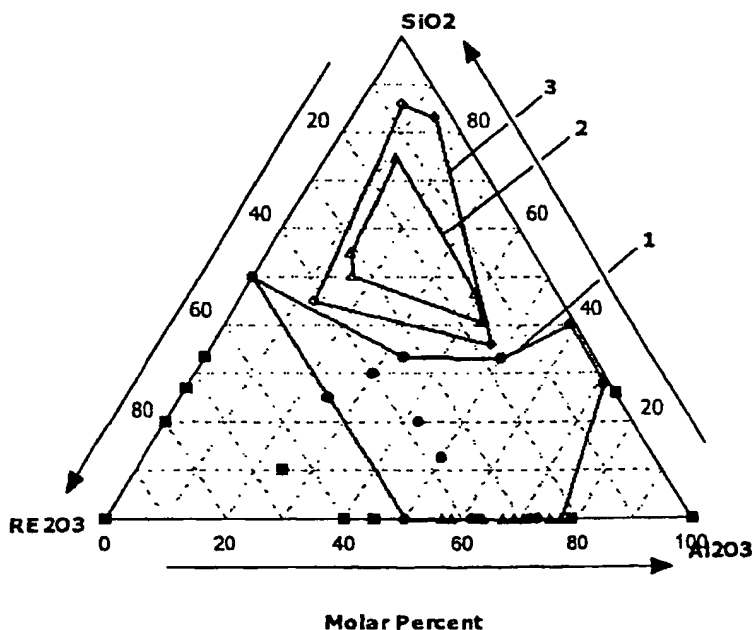
— Before the expiration of the time limit for amending the
claims and to be republished in the event of receipt of
amendments.

(71) Applicant: CONTAINERLESS RESEARCH, INC.
[US/US]; 906 University Place, Evanston, IL 60201 (US).

(72) Inventors: WEBER, J., K., Richard; 3090 Daniels Court,
Arlington Heights, IL 60004 (US). ABADIE, Johan, G.;
Apartment #2, 1221 West Barry, Chicago, IL 60657 (US).
HIXON, April, D.; 407 Wilder Drive SE, Cedar Rapids,

For two-letter codes and other abbreviations, refer to the "Guid-
ance Notes on Codes and Abbreviations" appearing at the begin-
ning of each regular issue of the PCT Gazette.

(54) Title: SINGLE PHASE RARE EARTH OXIDE-ALUMINUM OXIDE GLASSES



(57) Abstract: A bulk single phase glass comprising 23 molar % to 50 molar % rare earth oxides, RE₂O₃, and 50 molar % to 77 molar % aluminum oxide, Al₂O₃ is provided. The glass contains at least 50 molar % of Al₂O₃ + RE₂O₃ and smaller amounts of oxide glass forming agents and other oxides than are found in prior art glasses. The addition of small amounts of lanthanum oxide, La₂O₃, prevents phase separation. The single phase glass is useful for optical applications such as lasers and optical amplifiers.

Title

Single Phase Rare Earth Oxide-Aluminum Oxide Glasses

5

Statement Regarding Federally Sponsored Research or Development

This invention was made with U.S. government support under contract numbers NAS8-40847 and NAS8-98092 awarded by the National Aeronautics and Space Administration. The United States Government has certain rights in this invention.

Background

1. Field of the Invention

The present invention relates to homogeneous glass materials formed from rare earth oxides and aluminum oxide. In particular, the present invention relates to rare earth oxide-aluminum oxide glass compositions in which the addition of lanthanum oxide eliminates the phase separation observed in prior art glasses, allowing homogeneous glasses to be prepared. The invention also relates to homogeneous glasses formed by rare earth oxides and aluminum oxide that contain smaller amounts of the glass forming agents, SiO_2 and/or B_2O_3 than are used in prior-art glasses. Such glasses comprise mixtures of rare earth element oxides (RE_2O_3), i.e., oxides of the elements with atomic numbers of 21, 39, 57-71: Sc, Y, La, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, combined with aluminum oxide, Al_2O_3 , and, optionally, additives comprising oxides of other elements.

2. Description of the Prior Art

Glasses have numerous applications in sensors, electrical

insulators, instruments, optical devices, optical waveguides, and components that require uniform optical properties, uniform density, and freedom from asperities and defects that would cause light scattering. Glasses containing selected
5 rare-earth ions or "dopants", for example, Er, Nd, Yb, Pr, Ho, Eu, are of particular value due to their applications in lasers, amplifiers, optical switches, optical filters, and optical components for light transmission at ultraviolet, visible, and infra-red wavelengths. Compared to crystals,
10 glass "hosts" can enable much broader bandwidths and greater pulsed power output for laser transitions by providing a range of electronic environments for the laser active ions, thereby extending the range of wavelengths over which laser sources and amplifiers can be operated.

15 Much effort has been invested to develop glasses for commercial applications. The presence of random fluctuations (often called "striae") in composition, density, index of refraction and other properties makes a glass practically useless for optical applications, even window glass, due to
20 light scattering and the unpredictable optical path through the material. Striae, and other inhomogeneities, also limit the utility of a glass in applications where uniform mechanical and thermal properties are required. As a result, development of homogeneous, single-phase glasses has been a
25 priority. In addition, development of glasses with high refractive index, glass waveguides and fibers, infrared transmitting glasses, and filter glasses has been driven by continually increasing application requirements.

The prior art in oxide glass making can be described in
30 terms of the "families" of glass based on certain glass forming agents that are currently used. The prior art

"families" of glass are based on compositions which contain substantial amounts of one or more of the glass forming agents: silica, SiO_2 ; arsenic oxide, As_2O_3 ; boria, B_2O_3 ; germania, GeO_2 ; phosphorus oxide, P_2O_5 ; telluria, TeO_2 ; and
5 vanadia, V_2O_5 . The widely used silica-based crown and flint glass families were developed in the early 1900s by Schott and others. Germanate glasses (based on germanium oxide, GeO_2) were developed in the 1920s, phosphate glasses (based on phosphorus oxide, P_2O_5) were developed in the late 1930s.
10 Heavy metal borate glasses with high refractive index were developed by Morey in the 1940s. Tellurite glasses (based on tellurium oxide, TeO_2) were developed in the 1950s.

Prior art relating to rare earth aluminum oxide glasses includes Sedykh, et al. [Izvestiya Akademii Nauk SSSR, Neorganicheskie Materialy, Vol. 11, No. 6, pp. 1153-1154,
15 1975], who report glass forming compositions in the Y_2O_3 - Al_2O_3 - SiO_2 system. The glass forming composition with the least amount of SiO_2 that is reported by Sedykh, et al. contains 40.3 molar % SiO_2 , 43.4 molar % Al_2O_3 and 16.3 molar
20 % Y_2O_3 . The glasses reported by Sedykh, et al. contain from 16 to 33 molar % Y_2O_3 . Day and Ehrhardt, in US Patent No. 4,789,501, disclose glass microspheres containing aluminum oxide, yttrium oxide and silicon oxide. The compositions of the glass microspheres of Day and Ehrhardt, and of the bulk
25 glasses of Sedykh, et al. are within a region of the ternary Y_2O_3 - Al_2O_3 - SiO_2 composition diagram that is given in weight percent and converted to molar percent in Table 1.

Table 1

Range Of Compositions Of Oxide Glasses Disclosed in US Patent
No. 4,789,501

Component	Weight Percent				Molar Percent			
	A	B	C	D	A	B	C	D
SiO ₂	20	70	70	20	45	86	83	36
Al ₂ O ₃	10	10	20	45	13	7	14	47
Y ₂ O ₃	70	20	10	35	42	7	3	17

5

McPherson and Murray, in US Patent 5,747,397, also disclose glass containing rare earth oxides and aluminum oxide with additions of glass-forming agents and other oxides. The glasses disclosed by McPherson and Murray contain 30-70 molar
10 % of oxide glass forming agents (SiO₂, GeO₂, B₂O₃, and P₂O₅), 0-25 molar % of Al₂O₃, 20-42 molar % of RE₂O₃ (Y₂O₃, Er₂O₃, Nd₂O₃, La₂O₃, Gd₂O₃, and Yb₂O₃), and 0-28 molar % of other oxides (TiO₂, K₂O, ZrO₂, ZnO, Nb₂O₃, and Ga₂O₃). The glasses claimed by McPherson and Murray contained from 48-66 molar %
15 of TiO₂ + SiO₂ + GeO₂ + B₂O₃, i.e., no more than 52 molar % of Al₂O₃ + RE₂O₃. The compositions disclosed by McPherson and Murray contained no more than 55 molar % of Al₂O₃ + RE₂O₃.

Eberlin, in US Patent 2,206,081 discloses optical glasses comprised of heavy metal oxides and B₂O₃ as the glass forming
20 agent. The glasses disclosed by Eberlin contain 37-70 molar % of B₂O₃, no Al₂O₃, 10-32 molar % of La₂O₃, and 20-39 molar % of other oxides (ThO₂, Ta₂O₅, ZrO₂, Na₂O, and LiNO₃).

Glass materials with compositions in the range 24 molar % to 32 molar % Y₂O₃ with the balance Al₂O₃ have been reported
25 in the scientific literature. These yttrium oxide-aluminum

oxide glasses occur as a heterogeneous mixture of two different glasses that form when the liquid is rapidly cooled. A glass of 37.5 molar % Y_2O_3 in Al_2O_3 has also been reported, but we show here that this glass is also a mixture of two different glasses.

All of the rare earth elements and aluminum exhibit an oxidation state of +3. Four-, six-, and eight-coordination ionic radii for these ions are given in Figure 1. The horizontal lines in the figure are the cation radii for 4-, 6- and 8-coordination with O^{2-} ions at which the coordinated O^{2-} anions just touch, i.e., the "critical" radii for 4-, 6-, and 8-coordination with O^{2-} . According to Pauling's rules, the local coordination most likely to occur is that of the largest polyhedron for which the cation radius exceeds the critical radius.

The prior art also teaches that optical waveguides may be made from crystalline oxide materials, such as yttrium aluminum garnet (YAG) of composition $\text{Y}_3\text{Al}_5\text{O}_{12}$, with compositions similar to those of this invention.

Prior art glasses containing substantial amounts of rare earth oxides and aluminum oxide are either two phase glasses that are not suitable for optical applications, or they contain at least 30 molar % of the glass forming agents, SiO_2 and/or B_2O_3 .

Thus there exists a need for glasses that may readily be configured into optical waveguide forms and dimensions to be used in applications concerning guiding light waves for the purpose of operating optical devices such as lasers and optical amplifiers.

It is, therefore, an object of the invention to provide a

6

glass that can be used in optical applications where uniform mechanical and thermal properties are required.

Another object of the invention is to provide homogeneous, single phase glasses.

5 Yet another object of the invention is to provide glasses that have a high refractive index.

Description of the Figures

Figure 1 shows the radii of trivalent rare earth and aluminum cations in 4-, 6-, and 8- coordination with O^{-2} anions, and the critical radii for 4-, 6-, and 8-coordination with O^{-2} anions.

Figure 2 is a ternary composition diagram showing the compositions of glasses formed from mixtures of rare earth oxides, aluminum oxide, and silicon dioxide.

Figure 3 is a ternary composition diagram showing the molar compositions of glasses formed from mixtures of rare earth oxides, aluminum oxide, and other oxides.

Figure 4 shows the optical transmission of single phase glass of a composition comprised of 37.5 molar % La_2O_3 and 62.5 molar % Al_2O_3 .

Figure 5 shows the optical absorption spectrum of Er^{+3} ions in a single phase glass containing 1 molar % Er_2O_3 , 7 molar % La_2O_3 , 30.5 molar % Y_2O_3 and 61.5 molar % Al_2O_3 .

Summary

The present invention is a bulk single phase glass comprising (i) rare earth oxides and aluminum oxide or (ii) rare earth oxides, aluminum oxide, and oxides that are glass forming agents such as silicon dioxide, with up to 15 molar % of other oxides added to these glasses. The composition range of the glasses of this invention that contain RE_2O_3 and Al_2O_3 but no conventional glass forming agents such as silicon dioxide is from about 23 to 50 molar % of RE_2O_3 and from 77 to 50 molar % of Al_2O_3 . The composition range of the glasses of this invention that contain RE_2O_3 , Al_2O_3 , and silicon dioxide (or other oxides that are glass forming agents) lies substantially within a polygonal region of a ternary composition diagram of the rare earth oxide - aluminum oxide - silicon dioxide system where the region is defined by the range of compositions given in Table 2.

Table 2

Composition Range, molar %, of Glasses of this Invention

RE ₂ O ₃	Al ₂ O ₃	SiO ₂
1	59	40
1	71	28
23	77	0
50	50	0
50	0	50
33.33	33.33	33.33
16.67	50	33.33

Description of Invention:

The invention provides bulk forms of single phase glass made from materials containing oxides of aluminum and the rare earth elements. In the context of this invention, a "bulk single phase glass" means an amorphous material having macroscopic dimensions. The glass materials may exhibit variations in density, refractive index, chemical composition, or other physical and chemical properties over the dimensions of the glass material, but they may not exhibit discontinuities in these properties. They will have macroscopic dimensions, which as a practical matter means that the dimensions of the single phase glass exceed 0.01 cm in two orthogonal directions and 0.001 cm in the third orthogonal direction. These dimensions distinguish the bulk glasses of this invention from microscopic (non-bulk) glass materials such as fine particles, thin glass fibers, and thin amorphous coatings that may be formed by various means.

The glass materials disclosed in this invention were made by containerless techniques. The containerless techniques are a simple laboratory method to demonstrate glass formation, by eliminating contact between the melt and a solid container. This approach allows undercooling of the melt below the melting point of the crystalline phases and below the liquidus temperatures that occur in the oxide systems investigated. It avoids heterogeneous nucleation of crystalline material due to contact with a container, which would prevent the formation of glass.

The glass specimens were prepared by melting weighed mixtures of high purity Al_2O_3 , Er_2O_3 , La_2O_3 , Y_2O_3 or small pieces of pure YAG crystals, other rare earth oxides, and

oxides of other elements (obtained from Cerac, Inc., Milwaukee, Wisconsin, U.S.A.) in a laser hearth melter. The compositions of the mixtures are presented in Tables 3 to 7. The hearth melting process formed spheroidal samples of 0.1 - 0.35 cm in diameter that were subsequently levitated and melted. Glass was formed when the molten samples were allowed to cool at a sufficient rate.

Levitation of the spheroidal samples was accomplished using an aero-acoustic levitator (AAL) or a conical nozzle levitator (CNL). The samples were levitated, heated by continuous wave CO₂ laser beam heating, melted, and the melt was held at a temperature above the melting point for a period of time from a few seconds up to more than one minute after melting, then cooled immediately by turning off the laser power, or cooled to a lower hold temperature for a few minutes before cooling to room temperature. Sample temperatures were measured with an optical pyrometer. The cooling rates were determined from the temperature versus time data.

The glass samples were examined under a binocular microscope at a magnification of 15-60 and, after preparing polished sections of the glass, under a metallurgical microscope at 50-200 magnification to determine if they were homogeneous (single phase). Some of the samples, with compositions close to the limits on composition at which single phase or two phase glasses were formed, were cut and polished to allow more precise examination under a microscope.

The containerless techniques are not a requirement for making the glass of the present invention since the oxide melts of interest may, for example, be supported on a liquid that (i) has a density greater than the oxide liquids, (ii) has a melting point below the glass transition temperature of

11

the glass that is formed when the liquid oxide is cooled, and (iii) unlike solid containers, does not promote heterogeneous nucleation of crystalline material in the undercooled liquid oxides. Liquid tin has the required properties, and it is already widely used with prior art glass making as the supporting medium in float glass processes. Liquid gold may also be used to float the oxide liquids and glass materials of interest without contact with any solid material that would induce heterogeneous nucleation of crystals.

One method conceived for synthesis of large masses of the glass materials of this invention is:

(i) Melting the glass-forming oxide mixtures by heating to a desired temperature, typically above 2000°C. (Iridium is the preferred crucible material for melting of rare earth oxides and aluminum oxide.);

(ii) Heating and melting a pool of liquid gold or tin contained in a suitable melting crucible at a temperature above the melting point of the gold (1063°C) or the tin (232°C); and

(iii) Pouring the liquid oxide onto the liquid gold or tin to cool the oxide and form a mass of glass that floats on the liquid metal.

A second method to process larger masses of glass materials is to melt the glass forming oxide mixture in a crucible and cast the liquid oxide into a cooled metal die. It is possible that heterogeneous nucleation of crystals will occur at the glass surface where the liquid comes into contact with the die. However, if the cooling rate is large enough, i.e., if the casting is thin enough, glass will be formed before the crystals propagate through the casting thickness. Such crystals can be later removed by polishing of the surface

to obtain a homogeneous glass product.

A third method to process larger masses of glass materials is to use the gas film levitation method developed by Granier and Potard [J. Granier and C. Potard, Proc. 6th
5 Eur. Symp. Micrograv. Bordeaux, France, ESA SP-256 (1987), pp. 421-25, see also U.S. Patents 4,620,587, 4,617,084, 4,546,811, 4,539,173, 4,197,273, and 4,096,024, incorporated herein by reference]. The sample is levitated by floating on a thin gas film formed by gas flow through a porous membrane. A furnace
10 or EM heated graphite susceptor may be used to achieve high temperatures.

The glasses of the present invention are comprised of the oxides of aluminum and one or more of the seventeen rare earth elements. These eighteen elements are present in the glasses
15 as ions with a +3 charge. Four of these ions, Al^{+3} , Sc^{+3} , Y^{+3} , and La^{+3} , have electronic configurations equivalent to the rare gases, Ne, Ar, Kr, and Xe, respectively, except that the charge on the nucleus of the ion is three units greater than that of the corresponding rare gas. A fifth rare earth
20 ion, Lu^{+3} , has an electronic configuration similar to Xe, except that it includes a filled f-shell of electrons that is not optically active. Therefore, these five ions have optical properties similar to the rare gases, and glasses formed from the oxides of these ions will be transparent from the
25 ultraviolet to the mid-infrared region of the spectrum. The other thirteen rare earth ions that comprise the oxides used in the glasses of this invention have unpaired electrons in the 4f shell of electrons that lead to optical absorption within the ultraviolet to mid-infrared region of the spectrum.

30 Aluminum, yttrium, and lanthanum are relatively abundant and inexpensive elements, while scandium and lutetium are

relatively rare and expensive elements. The preferred embodiment of the invention is therefore a glass that is comprised of aluminum oxide and oxides of yttrium and/or lanthanum. Other rare earth oxides may be substituted for the yttrium oxide and/or lanthanum oxide. The glass may include additives of other oxides used to modify the processing characteristics and properties of the glass. The total concentration of these other oxides should be no more than 33 molar %, and preferably no more than 20 molar %.

The present invention is further defined in the following examples. It should be understood that these examples, while indicating various embodiments of the invention, are given by way of illustration only.

First Set of Examples

Table 3 summarizes the compositions of glasses prepared from mixtures of Al_2O_3 , Y_2O_3 , Er_2O_3 , La_2O_3 , and Nd_2O_3 in a first series of experiments. The table includes the molar percentages of the components, the cooling rates at which the glasses were formed (which were greater for smaller diameter samples), and whether the compositions were single phase. The cooling rates were determined in the temperature range from 1300-1400 K. Crystallization occurred spontaneously in the undercooled melts, at a temperature of approximately 1300 K, if the cooling rate was not sufficient to achieve glass formation. Examples I-A through I-S of Table 3 show compositions that resulted in a two-phase glass. The presence of two phases in the glass samples is undesirable for optical applications because it results in random scattering, reduced transmission, and distortion of the light traveling through the glass.

14
Table 3

Rare Earth Oxide - Aluminum Oxide Glass Compositions
Balance Al_2O_3 in all cases. * - estimated value

Example	Molar Percentages of Components				Cooling rate to form glass, °C/s	Single Phase
	Y_2O_3	Er_2O_3	La_2O_3	Nd_2O_3		
I-A	37.5				100-150	No
I-B	42.0				100-150	No
I-C	23.0				100-120*	No
I-D	37.4	0.1			80-130	No
I-E	36.5	1.0			100-150*	No
I-F	32.5	5.0			80-120	No
I-G		37.5			150-200*	No
I-H	37.4			0.1	75-120	No
I-J	36.5			1.0	100-150	No
I-K	32.5			5.0	80-120	No
I-L	37.4		0.1		100-150	No
I-M	37.0		0.5		100-150	No
I-N	36.5		1.0		100-150	No
I-O	35.5		2.0		100-120	No
I-P	34.0		3.5		80-130	No
I-Q		32.5	5.0		120*	No
I-R	32.5		5.0		<80	No
I-S	18.75	13.75	5.0		< 100*	No
I-T	27.5		5.0	5.0	<90	Yes
I-U		30.5	7.0		<90	Yes
I-V	27.5		10.0		<100	Yes
I-W	12.5	12.5	12.5		<70	Yes
I-X			37.5		<90	Yes
I-Y		10.0	40.0		100*	Yes
I-Z			50.0		<90	Yes
I-AA	27.0				<80	Yes
I-AB	30.0		7.0	0.5	< 120*	Yes
I-AC	28.5		9.0		< 120*	Yes

5

Examples I-T through I-AC show compositions that resulted in a single phase glass. The single phase glasses showed no evidence of phase separation either in visible light

15

transmission or by microscopic examination at magnifications of 15-60. The single phase glasses are brilliant, clear and transparent or colored and have excellent light transmission outside the absorption bands of the colored glasses. The Er-
5 containing glasses were pink-colored and the Nd-containing glasses were blue.

All but five of the compositions in Table 3 contain a ratio of aluminum oxide and rare earth oxides of 5:3, i.e., 62.5 molar % Al_2O_3 and 37.5 molar % of combined rare earth
10 oxides as RE_2O_3 . Examples I-B and I-C demonstrate the upper and lower limit respectively of yttrium oxide concentrations for $\text{Al}_2\text{O}_3:\text{Y}_2\text{O}_3$ compositions for which glass was obtained, i.e., from 42 to 23 molar % Y_2O_3 (58 - 77 molar % Al_2O_3). A small part of this composition range, near 27 molar % Y_2O_3 (73
15 molar % Al_2O_3) formed a single phase glass, as shown by example I-AA. Examples I-Y and I-Z demonstrate single phase glasses containing La_2O_3 , with 50 molar % RE_2O_3 and 50 molar % Al_2O_3 .

Examples I-T to I-AC demonstrate that single-phase glass
20 can be obtained at $\text{RE}_2\text{O}_3:\text{Al}_2\text{O}_3$ ratios in the range from 27:73 (Example I-AA) to 1:1 (Examples I-Y and I-Z). The single phase glasses contain a molar percentage of La_2O_3 that increases with the $\text{RE}_2\text{O}_3:\text{Al}_2\text{O}_3$ ratio. Thus, at $\text{RE}_2\text{O}_3:\text{Al}_2\text{O}_3 = 27/73, 3/5, \text{ and } 1/1$, the La_2O_3 content at which single phase
25 glass was obtained equals 0, at least 5, and at least 40 molar percent, respectively. We conclude that addition of La_2O_3 to compositions over the full range of glass formation will allow single phase glass to be obtained, and that the lower limit for the $\text{RE}_2\text{O}_3:\text{Al}_2\text{O}_3$ ratio at which single phase glass can be

16

made is therefore at or below a value equal to 23:77, as given by example I-C. In summary, we have found that a single phase glass can be produced from a melt having a composition of 23 - 50 molar % RE_2O_3 and 77 - 50 molar % Al_2O_3 , where 0 - 50 molar % of the rare earth oxide - aluminum oxide mixture is La_2O_3 .

Cooling Rate Data

All of the cooling rates given in Table 3 exceed the critical cooling rate for glass formation, R_C . R_C is defined as the minimum cooling rate at which glass can be formed free from crystalline material that can spontaneously nucleate in the undercooled liquid. Where a range of values or a single specific value is given for the cooling rate, crystallization was observed at slower cooling rates, i.e., the value of R_C was somewhat less than the minimum cooling rate given in the Table. Where an upper limit is given for the cooling rate, the cooling rates are an upper limit on R_C because smaller cooling rates were not achieved in the free-cooling experiments that were performed. These samples did not crystallize at any cooling rate achieved in the experiments. Estimated values of the cooling rate (marked with an asterisk) are given where the temperature versus time was not measured during the experiments. The results in Table 3 show that in general the value of R_C decreases with an increase in the lanthanum content of the glass.

Second Set of Examples

Table 4 presents the compositions of glasses prepared from mixtures of Al_2O_3 , Y_2O_3 , La_2O_3 , and ten other rare earth oxides. Examples II-A to II-R in Table 4 demonstrate that a

17

single phase rare earth oxide - aluminum oxide glass can be formed from compositions consisting essentially of 37.5 to 38.5 molar % rare earth oxides as RE_2O_3 and 61.5 to 62.5 molar % Al_2O_3 . Rare earth oxides not included in the table are

5 oxides of Ce, Pm, Gd, Dy, and Lu. However, because the properties of these elements are very similar to the properties of rare earth elements that were used, it is evident that these other rare earth oxides may also be used to form the single phase glasses of this invention. Examples II-S
10 and II-T show additional compositions that formed two-phase glasses.

Table 4

Rare Earth Oxide - Aluminum Oxide Glass Compositions

Example	Chemical Composition, Molar Percent					Single
	Y ₂ O ₃	La ₂ O ₃	Al ₂ O ₃	Other RE ₂ O ₃		Phase
II-A	16.5	10	62.5	1 Er ₂ O ₃	10 Yb ₂ O ₃	Yes
II-B	11	10	62.5	1.5 Er ₂ O ₃	15 Yb ₂ O ₃	Yes
II-C	6.6	10	62.5	1 Er ₂ O ₃	20 Yb ₂ O ₃	Yes
II-D	5.5	10	62.5	2 Er ₂ O ₃	20 Yb ₂ O ₃	Yes
II-E		25	62.5	12.5 Sc ₂ O ₃		Yes
II-F	29.5	7	62.5	1 Pr ₂ O ₃		Yes
II-G	29	7	62.5	1.5 Pr ₂ O ₃		Yes
II-H	27.5	7	62.5	3 Pr ₂ O ₃		Yes
II-J	30.5	7	61.5	1 Yb ₂ O ₃		Yes
II-K	30.5	7	61.5	1 Tm ₂ O ₃		Yes
II-L	30.5	7	61.5	1 Er ₂ O ₃		Yes
II-M	30.5	7	61.5	1 Ho ₂ O ₃		Yes
II-N	30.5	7	61.5	1 Tb ₂ O ₃		Yes
II-O	30.5	7	61.5	1 Eu ₂ O ₃		Yes
II-P	30.5	7	61.5	1 Sm ₂ O ₃		Yes
II-Q	30.5	7	61.5	1 Nd ₂ O ₃		Yes
II-R	30.5	7	61.5	1 Pr ₂ O ₃		Yes
II-S	30.25		58.0	4.5 Sc ₂ O ₃	7.25 Yb ₂ O ₃	No
II-T			62.5	37.5 Yb ₂ O ₃		No

Third Set of Examples

Table 5 presents data for a third set of glass samples, both those that underwent phase separation and those that did not. These glass samples were polished and examined under a metallurgical microscope at a magnification of 50-200 to more precisely examine the material for the presence of a second glass phase.

Table 5

Phase Separation In Polished Glass Specimens

* - estimated value

Example	Chemical Composition				Cooling		
	Molar Percent				Diam. mm	Rate °C/s	Single Phase
	Al ₂ O ₃	Y ₂ O ₃	La ₂ O ₃	RE ₂ O ₃			
III-A	62.5	30.5	7		3.5	100*	No Clear
III-B	62.5	30.5	7		3	125	No Clear
III-C	62.5	30.5	7		2.5	140	No Clear
III-D	62.5	30.5	7		2	175	Yes Clear
III-E	62.5	30.5	7		1.5	300	Yes Clear
III-F	62.5	29.5	7	1 Yb ₂ O ₃	3.6	95*	No Clear
III-G	62.5	29.5	7	1 Er ₂ O ₃	3.4	105*	No Pink
III-H	62.5	29.5	7	1 Tb ₂ O ₃	3.2	115*	No Yellow
III-J	62.5	29.5	7	1 Eu ₂ O ₃	3.0	125*	Yes Yellow
III-K	62.5	29.5	7	1 Pr ₂ O ₃	3.0	125*	No Yellow
III-L	62.5	29.5	7	1 Sm ₂ O ₃	2.7	135*	Yes Clear
III-M	62.5	29.5	7	1 Ho ₂ O ₃	2.5	140*	Yes Pink
III-N	62.5	29.5	7	1 Nd ₂ O ₃	2.5	140*	Yes Blue
III-O	62.5	29.5	7	1 Tm ₂ O ₃	2.4	145*	Yes Clear

In examples III-A through III-E the ratio of Al₂O₃ to total RE₂O₃ was 5:3, with 7 molar % La₂O₃ and 30.5 molar % Y₂O₃. These samples were prepared from liquid drops of

different diameters that exhibited a range of cooling rates as shown in the table. It can be seen that some phase separation could be observed in the larger glass samples which formed at smaller cooling rates. Small particles of the second glass phase were observed near the center of the samples, where the sample cooled at a slightly smaller rate than was measured at the sample surface and is reported in the Table. The size of the second phase particles decreased as the cooling rate increased, and no second phase was observed at cooling rates equal to or greater than 175°C/s.

Glass samples III-F through III-O were of the same composition except for the substitution of 1 molar % of Yb, Er, Tb, Eu, Pr, Sm, Ho, Nd, and Tm oxides for an equal amount of the Y₂O₃ content of the samples. In examples III-F to III-O, two each of the various glass materials were prepared and examined, to obtain the results stated in the column labeled "Single Phase". As with examples III-A to III-E, the observation of phase separation correlates with the sample size, i.e., with the cooling rate. In all examples, larger cooling rates gave single phase samples as determined by the microscopic examination of polished glass samples. It is evident that a slight further increase in the cooling rate or in the lanthanum content of the samples will allow single phase glass to be obtained for samples containing 1 molar % of Yb, Er, Tb, Eu, Pr, Sm, Ho, Nd and Tm oxides and RE₂O₃:Al₂O₃ ≈ 3:5.

Fourth Set of Examples

Table 6 presents the compositions of single phase glasses

prepared from mixtures of Al_2O_3 , Y_2O_3 , La_2O_3 , Er_2O_3 , and the non-rare earth oxides CaO , TiO_2 , SiO_2 , and ZrO_2 . Examples IV-A to IV-M demonstrate that a bulk single phase glass can be formed from compositions comprising 1.0 to 50 molar % RE_2O_3 , 0 to 71 molar % Al_2O_3 , 0 to 35 molar % SiO_2 , and 0 to 15 molar % other oxides. Since SiO_2 can have a deleterious effect on the optical properties of the glass, preferably the total concentration of SiO_2 is less than 35 molar %, and optimally the concentration of SiO_2 is zero. Alternatively, a useful bulk single phase glass has been obtained where the total concentration of RE_2O_3 and Al_2O_3 is at least 55 molar %. The table includes cooling rates measured for examples IV-E, IV-F, IV-J, IV-K, and IV-L.

Table 6
Single Phase Glass Compositions

Example	Chemical Composition						Cooling
	Molar Percent						Rate
	Y ₂ O ₃	La ₂ O ₃	Er ₂ O ₃	Al ₂ O ₃	SiO ₂	Other Oxides	°C/s
IV-A	17.5	10		57.5		10 CaO, 5 ZrO ₂	
IV-B	9.5	10	8	62.5		5 TiO ₂ , 5 ZrO ₂	
IV-C	30.5	5	2	42.5	20		
IV-D	37.5			50	12.5		
IV-E	1.0			59	40		300
IV-F	1.0			71	28		800
IV-G	40			30	30		
IV-H	50			25	25		
IV-J	50				50		800
IV-K	33.3			33.3	33.3		< 100
IV-L	16.7			50	33.3		< 100
IV-M	29.0	3.0		66.0		2 TiO ₂	

Composition Range of Single Phase Glasses

Figure 2 is a ternary composition diagram that illustrates the chemical compositions in molar % of single phase glasses formed from RE_2O_3 , Al_2O_3 , and SiO_2 .

5 Compositions of single phase glasses disclosed here are shown as filled circles. Compositions of two-phase glasses that will yield single phase glasses when the RE_2O_3 content includes sufficient La_2O_3 are shown as filled diamonds. Compositions that did not yield glass but instead crystallized upon cooling
10 of the liquid are shown as filled squares. Outlined region 1 in Figure 2 illustrates the range of compositions for the single phase glasses of this invention. Prior art glasses reported by Sedykh, et al. are shown as open triangles and outlined region 2. Compositions of prior art glasses of Day
15 and Ehrhardt (US Patent 4,789,501) are shown as open diamonds and outlined region 3. Not all of the compositions of the prior art glasses are shown in the figure, but all of the compositions of these glasses were within the borders 2 and 3 drawn by connecting the compositions that are presented in the
20 figure.

Figure 3 is a ternary composition diagram that shows the ranges of molar percentages of rare earth oxides, aluminum oxide, and all other oxides contained in the glasses disclosed here and in prior art glasses. Border 4 represents the glasses
25 disclosed by Sedykh, et al., comprised of Y_2O_3 , Al_2O_3 , and SiO_2 . Border 5 represents the glasses disclosed by Day and Ehrhardt, also comprised of Y_2O_3 , Al_2O_3 , and SiO_2 . Border 6 represents the glasses disclosed by Eberlin, comprised of La_2O_3 , B_2O_3 , Ta_2O_5 , ThO_2 , ZrO_2 , LiNO_3 , and Na_2O . Border 7
30 represents the glasses disclosed by McPherson and Murray,

23

which comprised Al_2O_3 , the rare earth oxides, Y_2O_3 , Er_2O_3 , Nd_2O_3 , La_2O_3 , Gd_2O_3 , and Yb_2O_3 , the glass forming agents, SiO_2 , B_2O_3 , GeO_2 , and P_2O_5 , and other oxides TiO_2 , K_2O , ZrO_2 , ZnO , Ga_2O_3 , and Nb_2O_5 . Border 8 represents the glasses disclosed here, which comprised Al_2O_3 , the rare earth oxides Sc_2O_3 , Y_2O_3 , La_2O_3 , Pr_2O_3 , Nd_2O_3 , Sm_2O_3 , Eu_2O_3 , Gd_2O_3 , Tb_2O_3 , Ho_2O_3 , Er_2O_3 , Tm_2O_3 , and Yb_2O_3 , the glass forming agent, SiO_2 , and other oxides CaO , ZrO_2 , and TiO_2 . The CaO , ZrO_2 , and TiO_2 were used in amounts up to 15 molar % of the glasses. The filled circles, diamonds, and squares represent compositions of single phase glasses, two phase glasses, and liquids that crystallized upon cooling of the liquid and did not form glass, respectively.

Relationship Between Cooling Rates and Glass Composition

The cooling rates employed to investigate glass formation from pure Y_2O_3 - Al_2O_3 compositions (see Table 2, Examples I-A to I-C and I-AA) were no greater than 150°C/s .

Crystallization of the melt always occurred outside the range of compositions (from 23 to 42 molar % Y_2O_3) for which glass was obtained when the melt was cooled at a rate less than 150°C/s . It is evident that the range of compositions for which glass was formed was limited by the cooling rate achieved in the glass synthesis experiments and that this range can be increased if means to increase the cooling rate are employed. Formation of glass from compositions containing at least 5 molar % La_2O_3 did not encounter limitations due to crystallization at the cooling rates that were used. The composition range of RE_2O_3 - Al_2O_3 glasses can be extended by

using La_2O_3 concentrations that were not investigated and by using larger cooling rates during the glass forming process.

It is known that, for oxide glass and metallic glass, a reduction in critical cooling rate, R_C , for glass formation may be obtained by adding multiple components to the glass-forming melt. In this way, a lower melting composition, such as a eutectic, can occur, allowing a lowering of the liquidus temperature and achieving glass formation before the liquid is sufficiently undercooled that crystallization occurs in the melt. Such a eutectic occurs in the $\text{Y}_2\text{O}_3 - \text{Al}_2\text{O}_3 - \text{SiO}_2$ system and contributes to the reduced cooling rates at which glass was obtained in Examples IV-K and IV-L relative to Examples IV-E, IV-F, and IV-J.

Means to increase the cooling rate and extend the composition range in which single phase glasses of this invention may be made would include using smaller diameter or thinner molten regions that achieve more rapid cooling rates. Increased cooling rates can also be obtained, without inducing heterogeneous nucleation, by pouring the liquid onto the surface of a cooler liquid such as liquid tin (melting point 505 K) or liquid gold (melting point 1336 K), or by die-casting.

Fifth Set of Examples

Single- and two-phase glass compositions selected from Tables 3-5 with $\text{RE}_2\text{O}_3:\text{Al}_2\text{O}_3 = 3:5$ are given in Table 7. The table also gives the average radius of trivalent rare earth ions, 8-coordinated with O^{2-} , for each composition. The example numbers are given in the first column, where it may be seen that one new example V-A is included. This glass, of

25

composition $\text{Gd}_2\text{O}_3:\text{Al}_2\text{O}_3 = 3:5$ was prepared after the correlation of average radius with single- and two-phase glass formation was discovered in the previous results.

26
Table 7

Selected Compositions That Form Single Or Two-phase Glasses
(62.5 molar % Al_2O_3 in all cases)

Example	Chemical Composition, Molar %			Ave. RE radius,	Phases
	La_2O_3	Y_2O_3	Other RE_2O_3		
II-T			37.5 Yb_2O_3	0.0858	2
I-G			37.5 Er_2O_3	0.0881	2
I-A		37.5		0.0892	2
I-F		32.5	5 Er_2O_3	0.1013	2
I-A		37.5		0.1015	2
I-Q	5.0		32.5 Er_2O_3	0.1024	2
I-S	5.0	18.75	13.75 Er_2O_3	0.1028	2
I-P	3.5	34.0		0.1030	2
I-R	5.0	32.5		0.1037	2
II-D	10.0	5.5	2.0 Er_2O_3 20 Yb_2O_3	0.1040	1
II-C	10.0	6.5	1.0 Er_2O_3 20 Yb_2O_3	0.1040	1
I-U	7.0	30.5		0.1046	1
I-T	5.0	27.5	5.0 Nd_2O_3	0.1051	1
I-AC	9.0	28.5		0.1055	1
I-V	10.0	27.5		0.1059	1
V-A			37.5 Gd_2O_3	0.106	1
I-W	12.5	12.5	12.5 Er_2O_3	0.1065	1
II-E	25.0		12.5 Sc_2O_3	0.1077	1
I-X	37.5			0.1180	1

5

The results in Table 7 show that the two-phase and single phase glasses occur in two groups for which the average radius values are less or greater, respectively, than approximately 0.1039 nm. This value is very close to the "critical radius" for 8-coordination with O^{2-} ions, 0.1020 nm, where the oxygen ions surrounding an 8-coordinated cation just touch. It follows, therefore, that the tendency to form a single phase glass from mixtures of rare earth oxides and aluminum oxide is greater if the average rare earth ion radius is large enough to favor 8-coordination with oxygen ions.

15 A useful rule is thus obtained to guide the choice of

single phase compositions that will form single phase glasses. For example, according to the ion radii given in Figure 1, binary mixtures of Al_2O_3 with oxides of La through Tb, with $\text{RE}_2\text{O}_3:\text{Al}_2\text{O}_3 \approx 3:5$, should yield single phase glasses if the liquid is cooled at a rate sufficient to avoid spontaneous crystallization. This conclusion was verified by example V-A. Single-phase glasses containing the oxides of Dy through Lu, Y, and Sc, would require addition of one or more of the oxides from La to Tb. The minimum amounts of the added rare earth oxides can be estimated from the ion radii given in Figure 1.

Properties of the Glasses

Properties of the novel glasses of this invention are discussed below. It is already known that the two-phase glass of the $\text{Y}_3\text{Al}_5\text{O}_{12}$ composition begins to crystallize when it is heated to a temperature of approximately 1250K, which is close to the estimated value of the glass transition temperature. The bulk modulus measured for this glass is 108 ± 2.5 GPa, and the shear modulus is 54 ± 1.2 GPa. Since the chemical bonding is similar in the whole family of glasses, similar high moduli would be expected for the other glass compositions. The bulk and shear moduli of these glasses are large compared with prior art glasses.

The Vickers hardness of glasses containing 37.5 molar % La_2O_3 + 62.5 molar % Al_2O_3 is in the range 670-730. The Vickers hardness values for glass compositions containing 62.5 molar % Al_2O_3 , balance La_2O_3 and Y_2O_3 are in the range 800-900 for 3.5 and 5 molar % La_2O_3 , and 850-880 for 10 molar % La_2O_3 .

The results given in Tables 3 to 7 show that the glasses of this invention may contain a wide range of optically active

rare earth dopant concentrations in a host composition comprised of optically transparent components. The erbium and neodymium ions in these glasses are important optically active components used, for example, in erbium doped fiber amplifiers or Nd:YAG lasers that have broad commercial applications. 5 Rare earth ions that exhibit laser action when doped into glass hosts include trivalent ions of praseodymium, neodymium, promethium, samarium, terbium, holmium, erbium, thulium, and ytterbium. It is well known that liberal substitution of the rare earths for each other is possible in the crystal lattice sites of minerals. The substitution property of rare earths for each other makes it possible to prepare single phase glasses of this invention that are doped with a wide range of concentrations of these laser-active rare earth ions, either 10 singly or in combination.

Figure 4 illustrates the optical transmission of a glass containing 37.5 molar % La_2O_3 + 62.5 molar % Al_2O_3 , i.e., the glass of example I-X. All of the single phase glasses prepared from aluminum oxide, yttrium oxide, and lanthanum oxide exhibited nearly identical transmission over the 20 wavelength range shown in Figure 4. It can be seen that high transmission occurs at wavelengths up to 5.0 μm . The transmission of glasses containing the oxides of Er, Nd, Eu, Pr, Yb, Tm, Ho, and Sm showed absorption spectra characteristic of the +3 ions of these optically active rare 25 earth elements. For example, Figure 5 illustrates the absorption spectrum of Er^{+3} ions in a thin section from sample II-L that was cut and polished on both sides. The absorption spectrum shown in Figure 5 is corrected for the non-unit transmission at all wavelengths due to reflection losses and 30 absorption of the host glass at the ultraviolet end of the

spectrum.

The infrared transmission of the glass that is illustrated in Figure 4, is comparable to that of sapphire and it extends beyond the infrared cut-off wavelength of silica-based glasses. However, unlike sapphire, these glasses are isotropic materials that will not exhibit birefringence. Sapphire is birefringent, i.e., the polarization state of light changes upon transmission through a sapphire window. The absence of birefringence makes the glasses of this invention superior to sapphire for use in applications involving polarized light.

The refractive index, n , of the glass whose transmission is shown in Figure 4 can be calculated from the maximum transmission, which was equal to approximately 84% at a wavelength of 880 nm. The less than total transmission occurs because each surface of the polished glass disk used in the transmission measurements reflects a small fraction of the light. The reflection coefficient, r , is determined by the refractive index according to the equation $r = (n - 1)^2 / (n + 1)^2$. The transmission, τ , of the glass sample is then obtained from the equation $\tau = (1 - r)^2$. Using $\tau = 0.84$ we obtain $r = 0.083$ and a value of 1.81 for the refractive index.

Thus, the novel glasses of this invention present many opportunities to achieve technologically useful properties, either singly or in combinations, that are not available in prior art glasses. These useful properties include, for example, high hardness, high solubility of optically active ions, high softening temperature, high transmission at infrared wavelengths, high refractive index relative to typical silica-based optical glasses, high glass transition temperature, high modulus, and insensitivity to gases such as

water vapor that are present in the atmosphere.

We anticipate that there are many compositions and variations within the composition ranges from which we have demonstrated formation of single phase glasses and which will
5 be useful in various applications relating to optical materials, structural materials, hard non-crystalline materials and other areas where oxide glasses are used. Based on the results disclosed herein, extensions and modifications to compositions which might be envisioned and implemented
10 within this family of glass materials would be obvious to those skilled in the art of glass making.

We claim:

1. A bulk single phase glass comprising:
 - (a) 27 to 50 molar % RE_2O_3 ; and
 - 5 (b) 50-73 molar % Al_2O_3 ,where RE is one or more elements selected from the group consisting of Sc, Y, La, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb and Lu.
- 10 2. The glass of claim 1 comprising at least 5 molar % La_2O_3 .
3. The glass of claim 1 wherein 0 - 50 molar % of the glass is La_2O_3 .
- 15 4. The glass of claim 1 wherein RE is one or more elements selected from the group consisting of Y, La, Nd and Er.
5. The glass of claim 1 wherein RE is Y or La.
- 20 6. The glass of claim 5 further comprising additives of other oxides used to modify the properties of the glass.
7. The glass of claim 1 consisting essentially of RE_2O_3 and Al_2O_3 in the ranges stated therein.
- 25 8. The glass of claim 7 comprising at least 5 molar % La_2O_3 .
9. A bulk single phase glass comprising one or more rare earth oxides, aluminum oxide and silicon dioxide wherein the
30 composition lies substantially within the heptagonal region of

32

the ternary composition diagram of the rare earth oxide-alumina-silica system defined by points having the following molar percent compositions: 1% RE₂O₃, 59% Al₂O₃ and 40% SiO₂; 1% RE₂O₃, 71% Al₂O₃ and 28% SiO₂; 23% RE₂O₃ and 77% Al₂O₃; 50% RE₂O₃ and 50% Al₂O₃; 50% RE₂O₃ and 50% SiO₂; 33.33% RE₂O₃, 33.33% Al₂O₃ and 33.33% SiO₂; and 16.67% RE₂O₃, 50% Al₂O₃ and 33.33% SiO₂.

10. A bulk single phase glass consisting essentially of:
- 10 (a) 1 to 50 molar % RE₂O₃;
(b) 0 to 71 molar % Al₂O₃;
(c) 0 to 35 molar % SiO₂; and
(d) 0 to 15 molar % other oxides;
- wherein the total concentration of RE₂O₃ and Al₂O₃ is at
- 15 least 55 molar % and wherein RE is one or more elements selected from the group consisting of Sc, Y, La, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb and Lu.

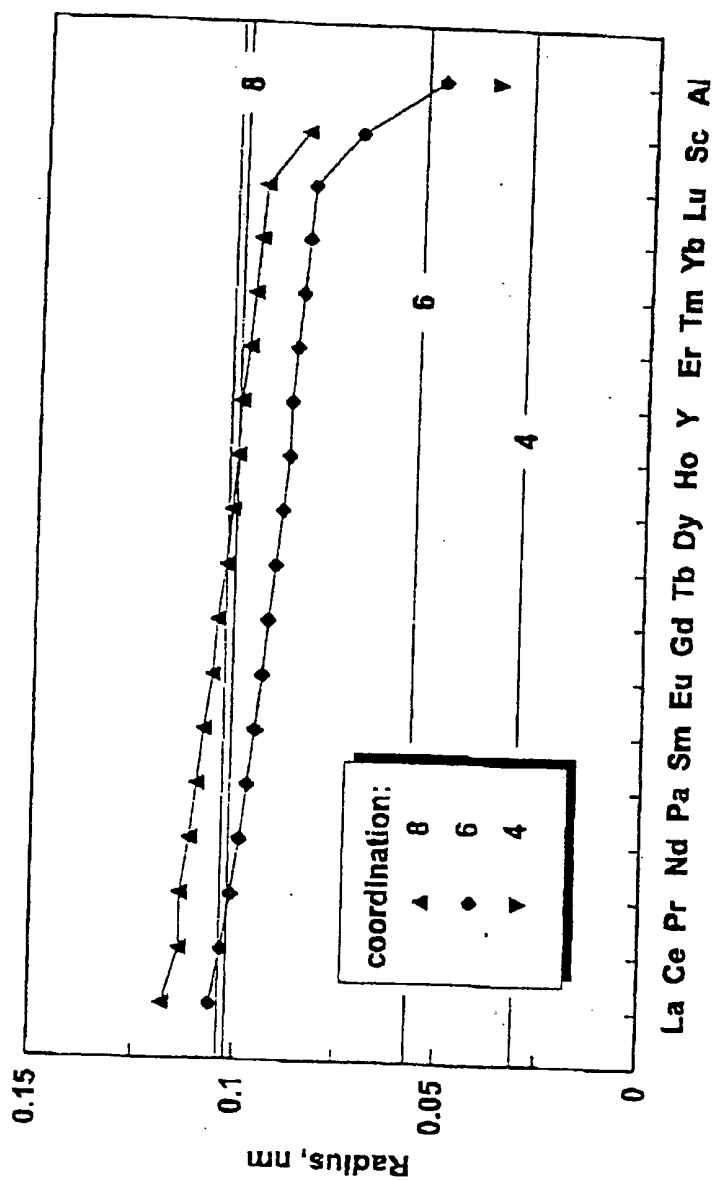


FIGURE 1

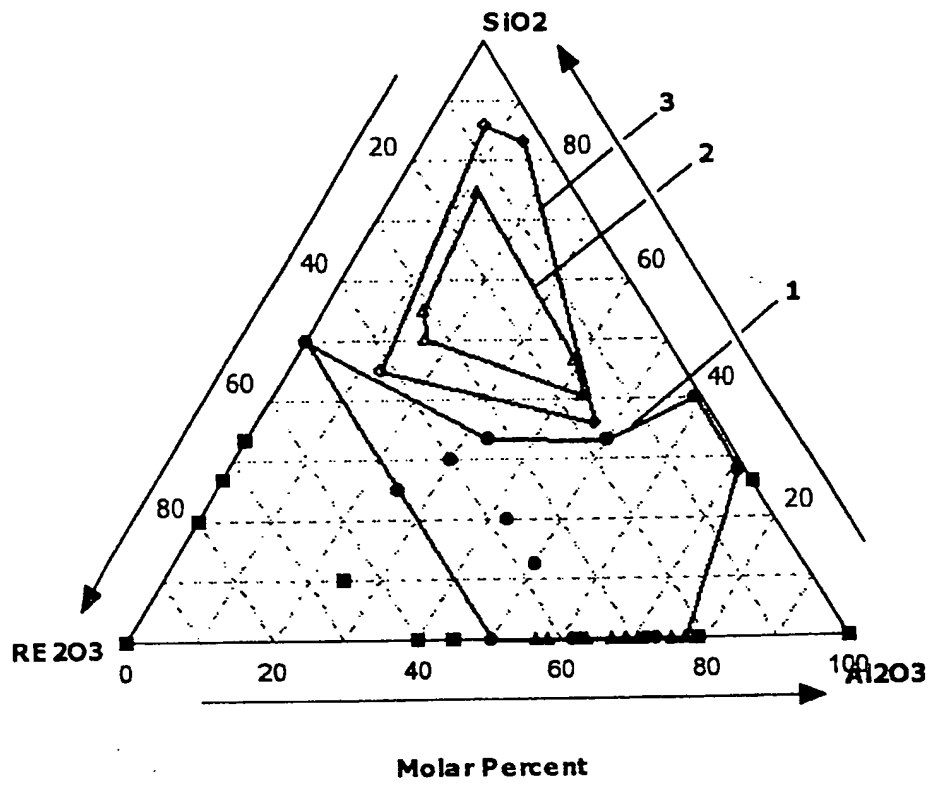


Figure 2

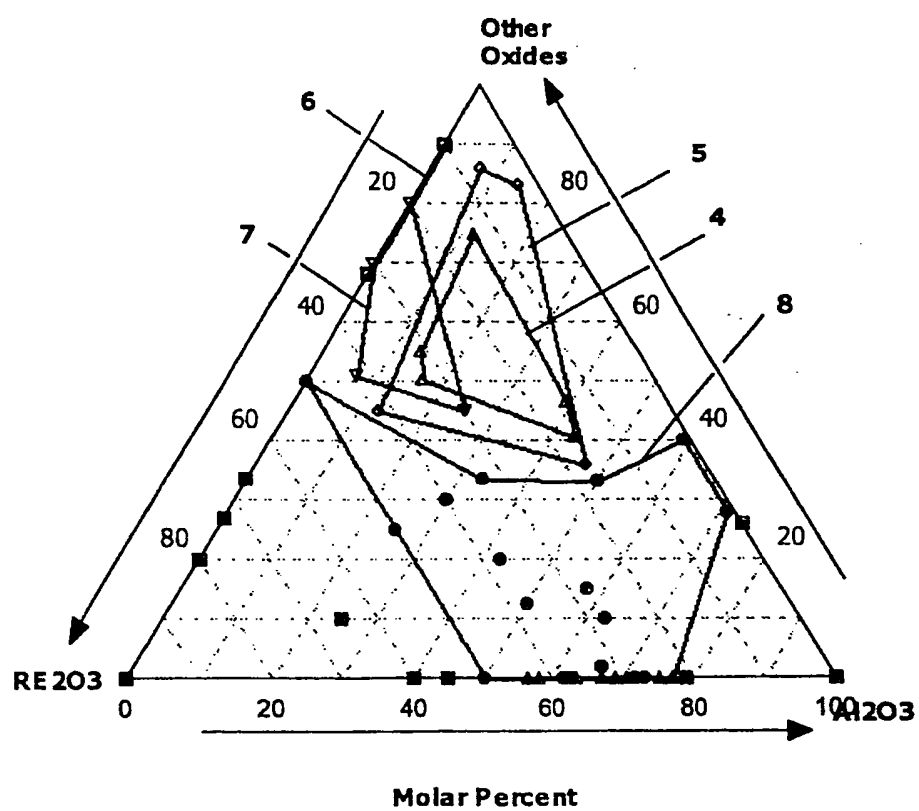


Figure 3

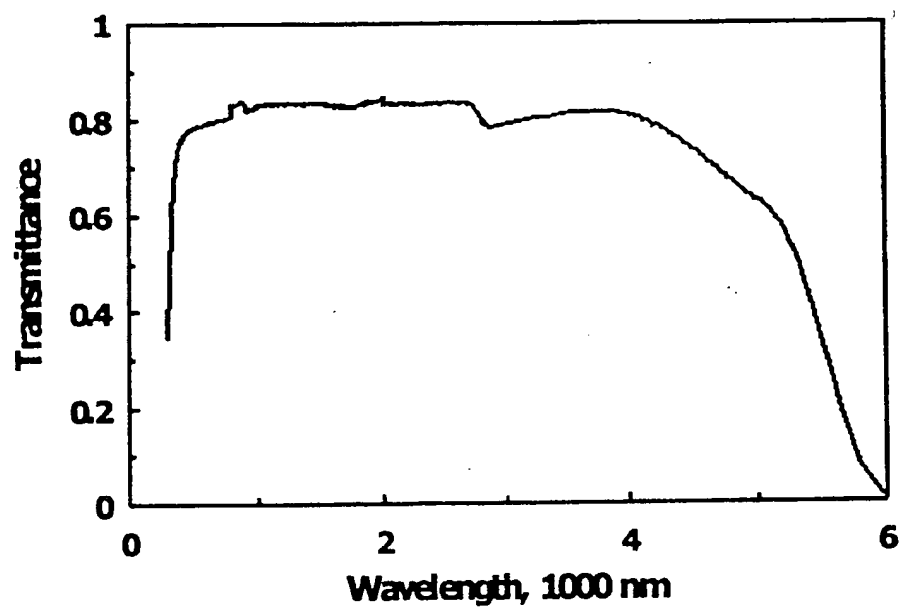


Figure 4

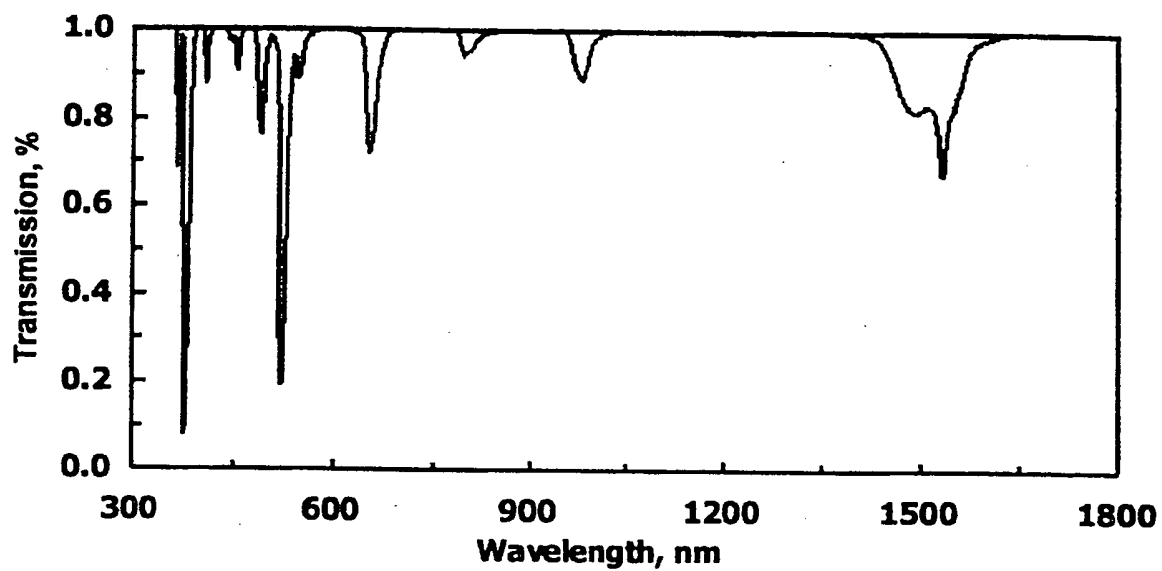


Figure 5

INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 00/28567

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C03C3/062 C03C3/068 C03C3/12 C03C4/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C03C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, IBM-TDB, INSPEC

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 97 25284 A (CONTAINERLESS RESEARCH INC) 17 July 1997 (1997-07-17) example 6; table I	1-10
X	WEBER J K R ET AL: "Glass fibres of pure and erbium- or neodymium-doped yttria-alumina compositions" NATURE, 25 JUNE 1998, MACMILLAN MAGAZINES, UK, vol. 393, no. 6687, pages 769-771, XP002160511 ISSN: 0028-0836 the whole document	1-10



Further documents are listed in the continuation of box C.



Patent family members are listed in annex.

* Special categories of cited documents:

- *A* document defining the general state of the art which is not considered to be of particular relevance
- *E* earlier document but published on or after the international filing date
- *L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- *O* document referring to an oral disclosure, use, exhibition or other means
- *P* document published prior to the international filing date but later than the priority date claimed

T later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

X document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

Y document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

g document member of the same patent family

Date of the actual completion of the international search

15 February 2001

Date of mailing of the international search report

02/03/2001

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel: (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+31-70) 340-3016

Authorized officer

Somann, K.

INTERNATIONAL SEARCH REPORT

Internat. Application No
PCT/US 00/28567

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
P,X	WEBER J K R ET AL: "Glass formation and polyamorphism in rare-earth oxide-aluminum oxide compositions" JOURNAL OF THE AMERICAN CERAMIC SOCIETY, AUG. 2000, AMERICAN CERAMIC SOC, USA, vol. 83, no. 8, pages 1868-1872, XP002160512 ISSN: 0002-7820 the whole document	1-10
X	US 5 747 397 A (MURRAY STEVEN C ET AL) 5 May 1998 (1998-05-05) cited in the application Sample ND-T10 table III	10
A	US 4 940 678 A (AITKEN BRUCE G) 10 July 1990 (1990-07-10) the whole document	1-10
A	ANONYMOUS: "Divalent Europium Glasses. July 1966." IBM TECHNICAL DISCLOSURE BULLETIN, vol. 9, no. 2, 1 July 1966 (1966-07-01), pages 117-118, XP002160513 New York, US the whole document	1-10
A	YUICHIRO MURAKAMI ET AL: "PHASE EQUILIBRIA AND PROPERTIES OF GLASSES IN THE AL ₂ O ₃ -YB ₂ O ₃ -SiO ₂ SYSTEM" JOURNAL OF THE CERAMIC SOCIETY OF JAPAN, INTERNATIONAL EDITION, JP, FUJI TECHNOLOGY PRESS, TOKYO, vol. 101, no. 10, 1 October 1993 (1993-10-01), pages 1071-1075, XP000416264 ISSN: 0912-9200 the whole document	1-10

BEST AVAILABLE COPY

INTERNATIONAL SEARCH REPORT

Information on patent family members

Internat. Application No

PCT/US 00/28567

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 9725284 A	17-07-1997	AU 1827097 A EP 0873282 A	01-08-1997 28-10-1998
US 5747397 A	05-05-1998	AU 5197898 A WO 9819974 A	29-05-1998 14-05-1998
US 4940678 A	10-07-1990	DE 4023399 A FR 2650266 A JP 3060440 A	31-01-1991 01-02-1991 15-03-1991

THIS PAGE BLANK (USPTO)